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HEAT PUMP TECHNOLOGIES FOR INDUSTRIAL APPLICATIONS

88-74-K

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ABSTRACT

This report outlines the various forms of closed-cycle heat pumping technologies being researched for use in high temperature industrial applications.

The two major classifications of heat pump technologies described in this report are mechanical and chemical heat pumps. Some current applications of high temperature industrial heat pumps are also outlined.

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EXECUTIVE SUMMARY

HEAT PUMP TECHNOLOGIES FOR INDUSTRIAL APPLICATIONS

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The intent of this report is to give an overview of the heat pumping technologies available to industry. The basic principles of operation of the various technologies are described in general terms. The less-common types of heat pumps are described in more detail than the types that have been in use by industry for significant lengths of time. The List of References at the end of the report contains sources of more detailed information on each type of heat pump.

In the mechanical heat pump section, two types of heat pump are discussed. The first, the compression heat pump, is a well-established technology which uses the change in entropy of a gas when it is compressed or expanded to pump heat. The second type, the magnetic heat pump, is a newer technique that has been applied mainly to low temperature (cryogenic) research applications. It uses the change in entropy of a magnetic solid when it is magnetized or demagnetized (the magnetocaloric effect). Recent research using more exotic magnetic materials has indicated promise in the higher temperature regions that are of interest to industry.

In the chemical heat pump section, four technologies are described. The first is the most common, the absorption heat pump. It uses the heat of mixing released when a refrigerant vapour is absorbed in or desorbed from a solvent. These pumps are suitable for a broad range of operating temperatures and have many attractive features for industry. The second type is the adsorption heat pump, which is much less common. It uses the condensation of gases, liquids, or dissolved substances on the surfaces of solids to pump heat. Because it is similar in operation and performance to the more common absorption heat pump, the adsorption heat pump has not received a great deal of study. Third in this section is the solution/dilution heat pump, which uses the exothermic dilution of water into an acid to pump heat. These pumps are already being used in a few industrial applications. The fact that concentrated acids are used requires adequate safety precautions, which are already standard in industry. Finally, the metal hydride heat pump is described. It has been given a great deal of attention in the last few years, but because it is a fairly new technology, it is not common in industry. Metal hydride heat pumps use the heat of reaction of a metal alloy when it absorbs/desorbs hydrogen to pump heat.

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The next section in the report describes the Peltier or thermoelectric heat pump, which cannot be classified as either mechanical or chemical. It uses the Peltier or reverse thermoelectric effect, which is the production or absorption of heat by a thermocouple when current is passed through it, to pump heat.

The last section of the report is an overview of all the technologies discussed, presenting the typical performance one could expect for each type of heat pump.

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To: Dr. D. Mills
Director of Research

HEAT PUMP TECHNOLOGIES FOR INDUSTRIAL APPLICATIONS

1.0 INTRODUCTION

In the past few years, many advancements have been made in a wide variety of heat pump technologies. Many of these technologies are suitable for industrial applications today. This report is intended to serve as an overview of the present state-of-the-art of heat pumps for industrial applications.

Sections 2 to 4 describe the various types of mechanical, chemical, and thermo-electric heat pumps. Section 5 is presents typical operating ranges and performance for each.

1.1 The Heat "Pumping" Principle

The principle of a heat pump is to remove heat from a low temperature stream (referred to as a source) and upgrade or "pump" this heat so that it may be transferred to a high temperature stream (referred to as a sink). This differs from heat exchangers which simply transfer heat from a high temperature source to a relatively lower temperature sink.

In industry, heat pumps are used to recover energy from waste energy streams. When waste energy is recovered and upgraded so that it may be returned to process applications, high grade energy forms, such as electricity, oil, and gas, may be conserved. Heat pumps provide an economical method for recovering heat that may otherwise be wasted.

1.2 Basic Categories for Industrial Heat Pumps

There are two general categories which industrial heat pumps are divided into - mechanical and chemical. Mechanical heat pumps convert a form of high grade energy, for example electricity or gas, to mechanical energy. This mechanical energy drives a compressor which compresses the unit's working fluid. Examples of a mechanical heat pump are the compression heat pump and the magnetic heat pump. Chemical heat pumps rely on solution/dilution, heats of reaction, heats of absorption, or the heat generated in phase changes in two or more compounds to boost the temperature of waste heat sources. Examples of chemical heat pumps include the absorption heat pump, the adsorption heat pump, and the metal hydride heat pump. A heat pump which does not fit neatly into either category is the thermoelectric, or Peltier heat pump, which uses the reverse thermoelectric effect.

2.0 MECHANICAL HEAT PUMPS

To upgrade waste energy from a low temperature stream to a high temperature stream, both mechanical and chemical heat pumps employ a working fluid (or fluids) to transfer and upgrade the energy received from a waste source. As mentioned in the beginning of this report, mechanical heat pumps convert a high grade form of energy to mechanical energy which drives a compressor or a moving magnet. The working fluid, which is sometimes referred to as a refrigerant, is circulated inside the heat pump, receiving heat from the source and the heat equivalent of the work input, and dispersing heat to the sink. The fluid can be made to undergo various cyclic processes. These cycles include the reverse Rankine, Stirling, Ericsson and Brayton cycles. Each of these cycles, along with the heat pump technologies using them, are described in the following paragraphs.

There are two methods of mechanical heat pumping which are being used or considered for industrial applications. The first type, the compression heat pump, has been well researched at relatively low temperatures in the past and is commonly found utilizing the reverse Rankine cycle in industrial applications. The second type, the magnetic heat pump, which shows great promise as an industrial heat pump in the future, is still in the preliminary research stage. Both of these mechanical heat pumping techniques are discussed in the following paragraphs.

2.1 Compression Heat Pumps

The compression heat pump, utilizing the reverse Rankine cycle is currently the most common heat pump found in industrial and residential applications. This heat pump is sometimes referred to as a vapour compression heat pump.

The pressure - enthalpy, temperature - entropy, and schematic diagrams of a reverse Rankine cycle heat pump are shown in Figure 1/1/. The 4 main processes may be clearly seen:

- 1->2: Heat is extracted from the source by boiling the refrigerant during a constant pressure (and temperature) heat addition.
- 2->3: The refrigerant vapour is then drawn into the compressor where it undergoes an isentropic (constant entropy) compression process to increase its pressure and temperature.
- 3->4: The heat from the compression process and the waste heat recovered from the evaporator is then discharged at the condenser when the refrigerant is condensed during the constant temperature process.
- 4->1: Once this heat has been released, the now liquid refrigerant passes through an expansion valve and returns to the evaporator, beginning a new cycle.

The major areas of reverse Rankine cycle technology in which research is being done are in increasing the current outlet temperatures to improve the overall efficiency of the system. Currently, Rankine cycle heat pumps are limited to maximum condensing temperatures of 120°C. Problems in refrigerant and lubricant stabilities which occur at elevated temperatures are now being researched. Therefore, the search for higher temperature working fluids and lubricants continues. There is also some effort being made to increase the efficiency and reliability of lubricant-free compressors, which would solve some of the problems with refrigerant/lubricant mixtures.

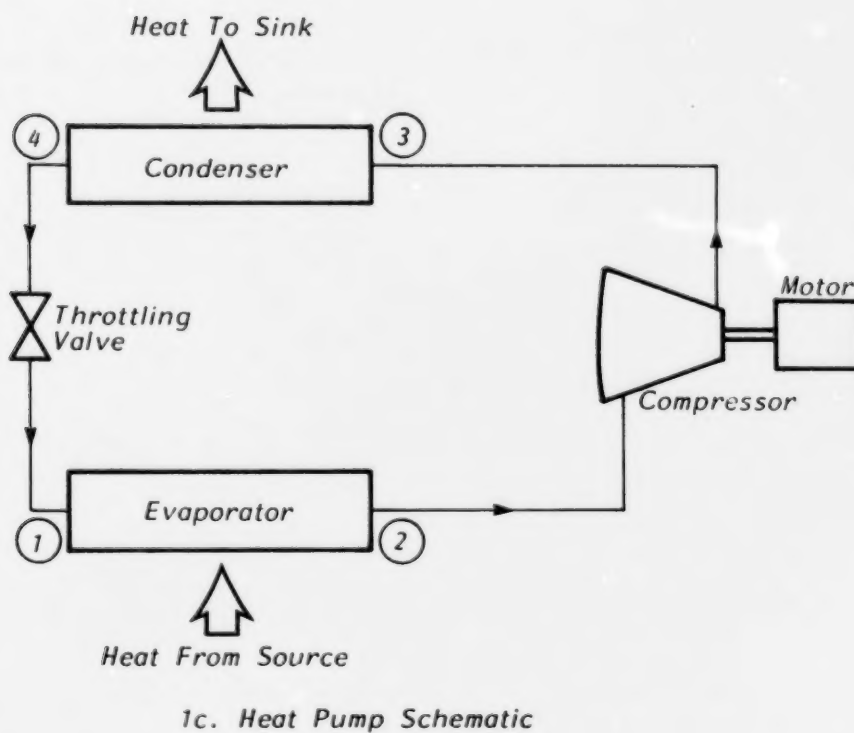
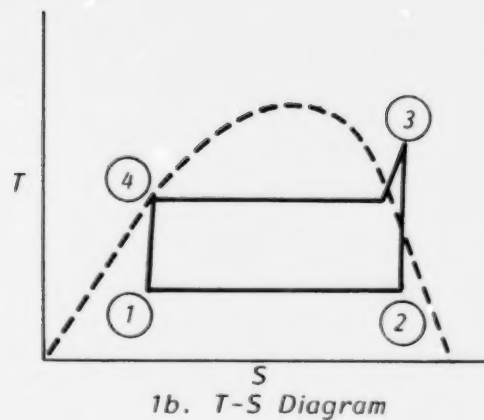
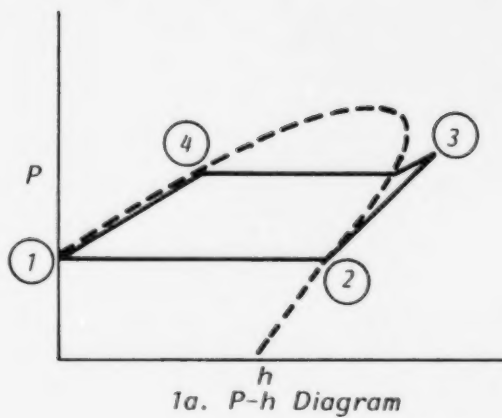


FIGURE 1
RANKINE CYCLE COMPRESSION HEAT PUMP

Reverse Rankine cycle heat pumps may use electricity or hydrocarbon fuels to drive the compressors. Electric motors have the advantage of being less expensive and more reliable than gas driven engines. However, gas engines have the advantage of utilizing the heat contained in their exhaust and cooling (oil and water) systems to increase overall efficiency. Whether an electric motor or internal combustion engine are used in a particular application depends on the relative price of their source of energy in the area of installation, and on the overall size of the unit. An internal combustion engine is the better driver for larger units.

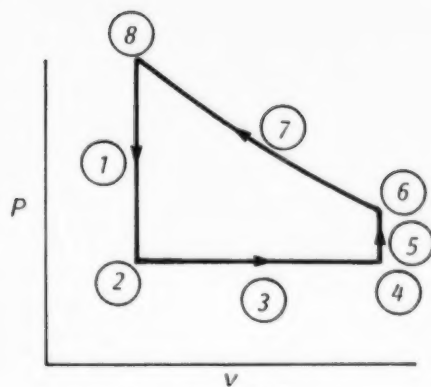
The reverse Stirling cycle, used in the Stirling cycle HP, is also currently under investigation as a future mechanical compression industrial heat pump cycle. The ideal Stirling cycle heat pump utilizes an ideal gas as a working fluid and involves two isothermal (constant temperature) processes and two isometric (constant volume) processes, as shown in the pressure - volume and temperature - entropy diagrams of Figure 2/2/. The reason for the interest in the Stirling cycle heat pump is that the theoretical efficiency of the Stirling cycle approaches that of the Carnot cycle between the same temperature limits when regeneration is used.

The Stirling cycle heat pump contains 3 primary components between which an ideal gas circulates. The three components are a hot side cylinder, a cold side cylinder, and a regenerator. The Stirling cycle, as shown in Figures 2 and 3, operates as follows/1,3/:

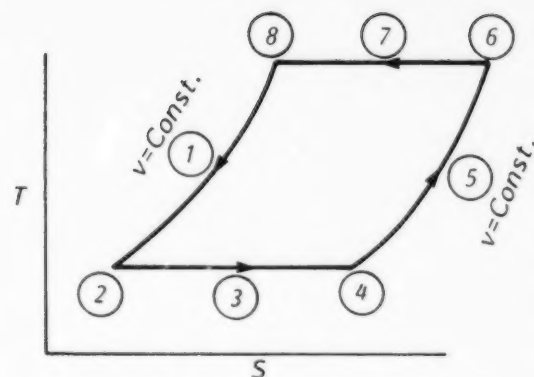
- 2->4: Heat is extracted from the source during the isothermal expansion process the isothermal conditions are maintained by increasing the volume of the working fluid (usually hydrogen or helium) in the system.
- 4->6: The temperature of the system is then increased during the isometric process by returning the energy extracted during the isometric process.
- 8->2: The process of returning previously extracted energy to the fluid is known as regeneration. Once the regeneration is complete, the heat from the working fluid is transferred to the sink during the isothermal compression process.
- 6->8: The temperature of the working fluid while transferring heat to the sink is kept constant by decreasing the volume of the working fluid in the system. The cycle is then completed by extracting waste energy from the fluid into the regenerator (8-12) which acts as temporary storage medium.

The reverse Ericsson cycle operates similarly to the Stirling cycle. The difference between the two cycles is that the reverse Ericsson cycle uses an isobaric (constant pressure) process during regeneration while the Stirling cycle uses an isometric (constant volume) process. The P-V and T-S diagrams for the reverse Ericsson air standard cycles are shown in Figure 4/2/

At present, there are no Stirling cycle heat pumps installed in industry. The reason for this is that the efficiencies that Stirling cycle HP's are currently attaining are less than those of reverse Rankine cycle heat pumps. This is due mainly to problems associated with maintaining constant temperature heat transfers, and to heat losses, regenerator inefficiencies and heat exchanger inefficiencies. It is most likely that an industrial Stirling cycle HP would utilize a diesel engine as the prime mover, because the heat from the exhaust stream can be recovered to increase the overall efficiency of the unit.



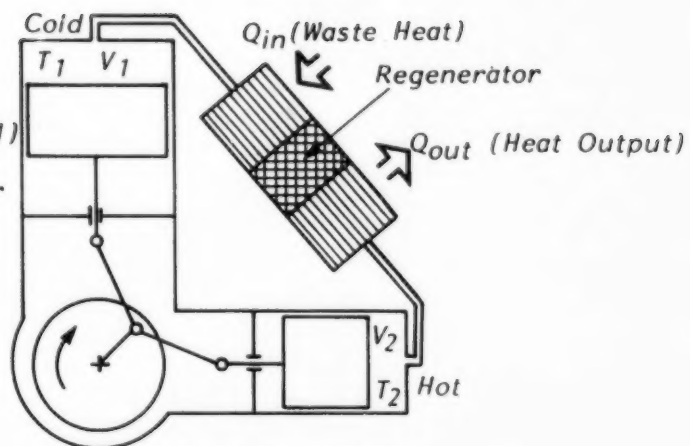
2a. P-v Diagram



2b. T-S Diagram

Stirling Heat Pump
Volume V_2 Lags V_1

Heat Source-Waste Heat at (1)
Heat Sink-Heat Out at (2)
Mechanical Drive - Displacer
Plus Net Work of
Compression



2c. Heat Pump Schematic

FIGURE 2
STIRLING CYCLE COMPRESSION HEAT PUMP

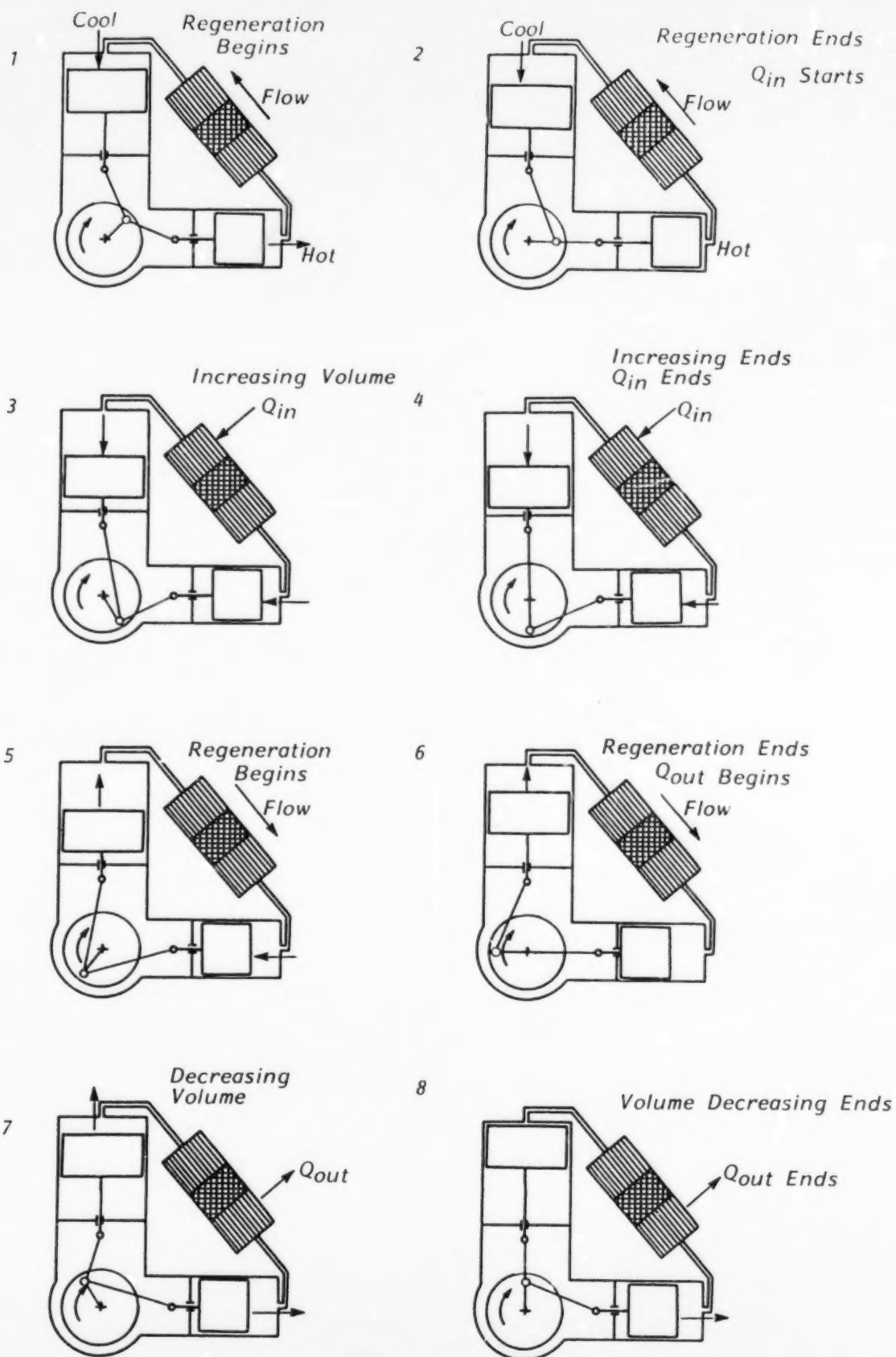


FIGURE 3
STIRLING CYCLE HEAT PUMP KINEMATICS
(STATE NUMBERS REFER TO GRAPHS OF FIGURE 2)

Current studies/4/ on the Stirling cycle heat pump indicate that a diesel powered semi-open Ericsson cycle concept, operating with helium as the working fluid, would be the most competitive configuration for industrial applications such as in the petroleum, paper, chemical and food processing industries.

The Brayton cycle is the ideal air standard cycle for gas turbines. The reverse Brayton cycle, referred to as a Brayton cycle heat pump, utilizes two isentropic and two isobaric processes. As shown in Figure 5a and 5b/2/:

- 1->2: Waste heat is absorbed into the working fluid (gas) during the isobaric process.
- 2->3: The working fluid then undergoes an isentropic compression process to elevate the temperature of the gas above the desired sink temperature.
- 3->4: The heat in the working fluid is then released to the sink during the isobaric process.
- 4->1: The working fluid completes the cycle by undergoing an isentropic expansion process through a turbine which produces some work to help drive the compressor.

The Brayton cycle heat pump, shown in its closed-cycle form in Figure 5c/2/, is not considered practical for most industrial applications. The Brayton closed-cycle heat pump has a substantially lower COP than that of the Rankine cycle operating between the same temperature limits, making the closed Rankine cycle heat pump a more practical solution in most applications. However, the Brayton cycle has a more stable COP than the Rankine cycle when the heat source temperature fluctuates widely/5/. The Brayton cycle heat pump is also considered better for open cycle applications, which eliminates one heat exchanger from the process. The best driver for the Brayton cycle heat pump is a gas turbine or diesel engine, because the heat may be recovered from the exhaust and returned to the process. This exhaust heat recovery increases the overall efficiency of the unit.

2.2 Magnetic Heat Pumps

In a demagnetized solid, the magnetic dipoles are aligned randomly. In this state, the entropy of the solid is a maximum. When it is magnetized, the dipoles become aligned. The amount of alignment is proportional to the strength of the magnetic field applied and to the external temperature. The magnetization thus reduces the entropy of the solid. If the magnetization is done under adiabatic conditions, the entropy reduction will result in an increase in temperature. Thus, the energy input to the system by magnetizing the material is "transformed" into heat. This principle, called the magnetocaloric effect, can be used to build a magnetic heat pump/6/.

The magnetocaloric effect is greatest when the temperature of the solid is near its Curie point/6,8/ which is the maximum temperature at which the material remains ferromagnetic. The maximum entropy change between magnetized and demagnetized states occurs at this point. Figure 6/6/ is a plot of the reversible adiabatic temperature change produced by a 7 Tesla magnetic field ($\sim 1 \text{ Mwh/m}^3$) as a function of initial temperature for gadolinium. It shows that most practical magnetic heat pumps should operate at a temperature near this point. Magnetic materials should be chosen with Curie points near the desired operating temperature. Suitable materials are available with Curie temperatures from near absolute zero to about $1100^\circ\text{C}/7/$.

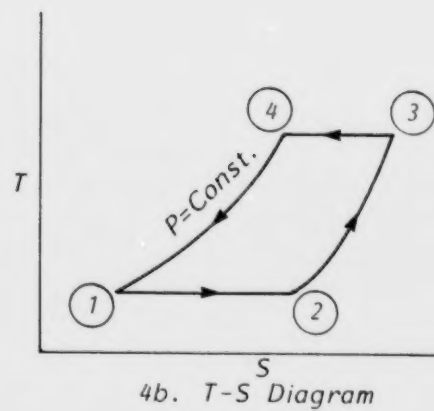
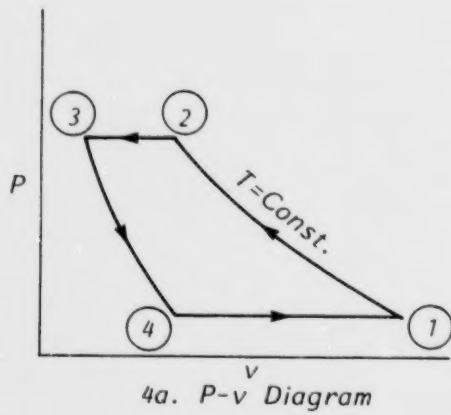
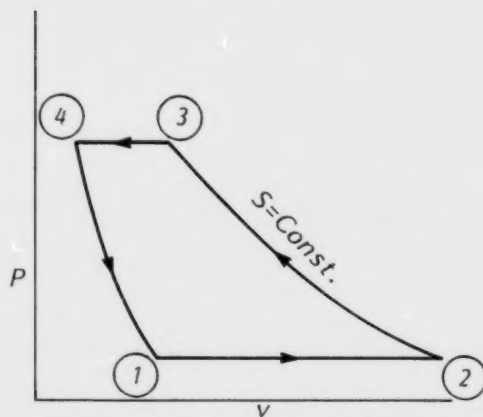
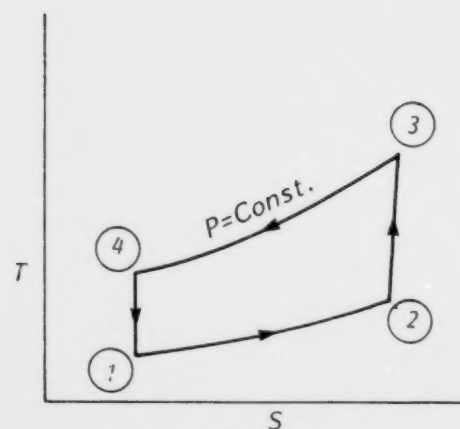


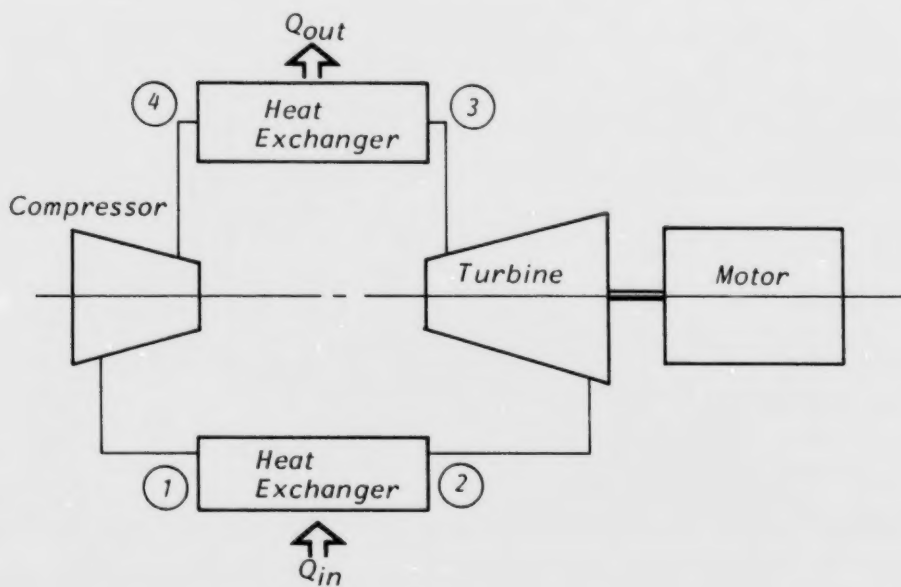
FIGURE 4
ERICSSON CYCLE COMPRESSION HEAT PUMP



5a. P-v Diagram



5b. T-S Diagram



5c. Heat Pump Cycle Schematic

FIGURE 5
BRAYTON CYCLE COMPRESSION HEAT PUMP

The best cycles for magnetic heat pumps are regenerative. One such cycle is the Brayton cycle (shown in Figure 7b) which is as follows/9/:

- 1->2: An adiabatic magnetization which raises the temperature of the magnetic material. The fluid at this point discharges its heat to the heat sink.
- 2->3: Cooling of the magnetic material against the regenerator fluid in a constant field.
- 3->4: Adiabatic demagnetization at the heat source. Fluid at this point picks up heat from the low temperature source.
- 4->1: Warming of the magnetic material from the regenerator fluid.

Another cycle used in magnetic heat pumps is the Stirling or Ericsson cycle shown in Figure 7d. It also has four steps as follows/9/:

- 1->2: Isothermal magnetization of the working material. The heat of magnetization is transferred, through the regenerator, to the heat sink.
- 2->3: Cooling of the magnetic material as it is moved through the magnetic field or the field is moved. The heat is carried off by the regenerator fluid, heating it.
- 3->4: Isothermal demagnetization, where heat is absorbed from the low-temperature heat source.
- 4->1: Zero-field warming of the material as it is moved back towards the high-temperature heat sink. The heat is absorbed from the regenerator fluid. Steps 2->3 and 4->1 are the regenerative sections of each cycle.

Most of the studies that have been done on magnetic heat pumps at temperatures useful to industry were performed using gadolinium (Gd) as the magnetic material/7/. Gd has a Curie temperature of 293K (20°C) which makes it ideal for room temperature heat pumping. It can become strongly magnetic, so it is an almost ideal magnetic material. One drawback is that it is relatively expensive.

The qualities required of the regenerator fluid are large heat capacity and low viscosity. Water is the best fluid that has yet been identified for this purpose/7/.

Two basic configurations of magnetic heat pumps have been proposed and tested in the laboratory. Dr. G.V. Brown of NASA Lewis/6,8,9/ has worked mainly with a reciprocating mechanism, and W.A. Steyert of the University of California/10/ has written papers on various rotary mechanisms.

The basic concept of a rotary magnetic heat pump as conceived by Steyert is shown in Figure 7a. The magnetic material is in the form of a rotating disc with the magnetic field applied to about half of it. The steps in the magnetic Brayton cycle are as follows/7/:

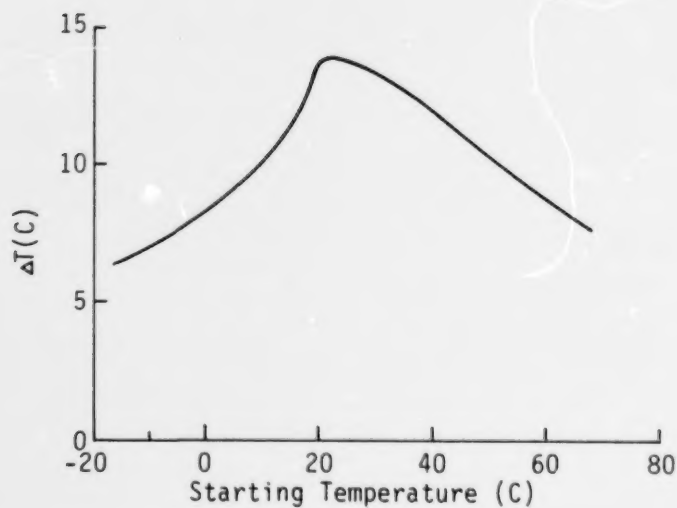
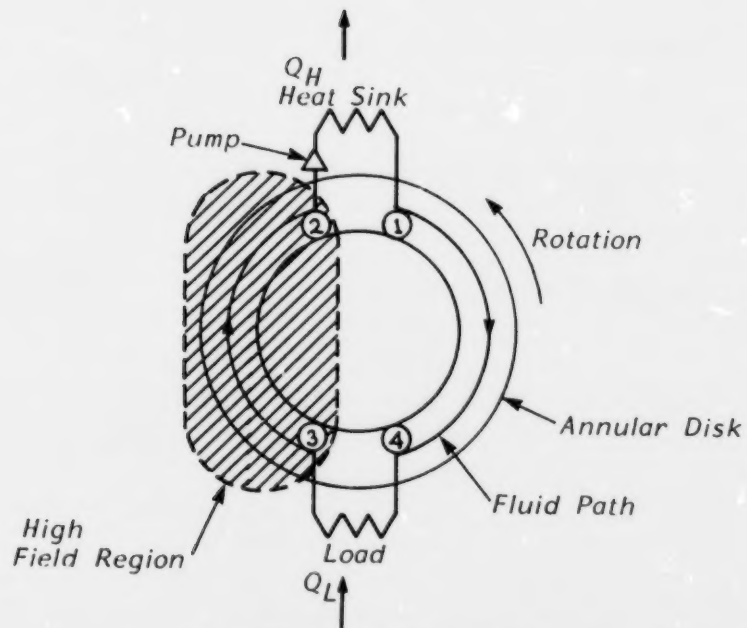
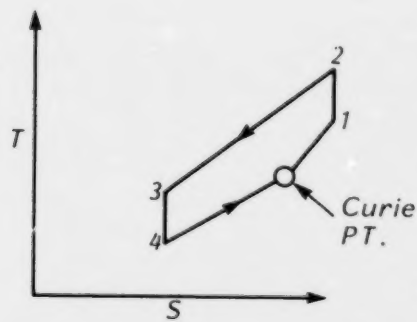


FIGURE 6
REVERSIBLE ADIABATIC TEMPERATURE
RISE ΔT PRODUCED BY APPLYING A 7 TESLA
FIELD AS A FUNCTION OF INITIAL TEMPERATURE T

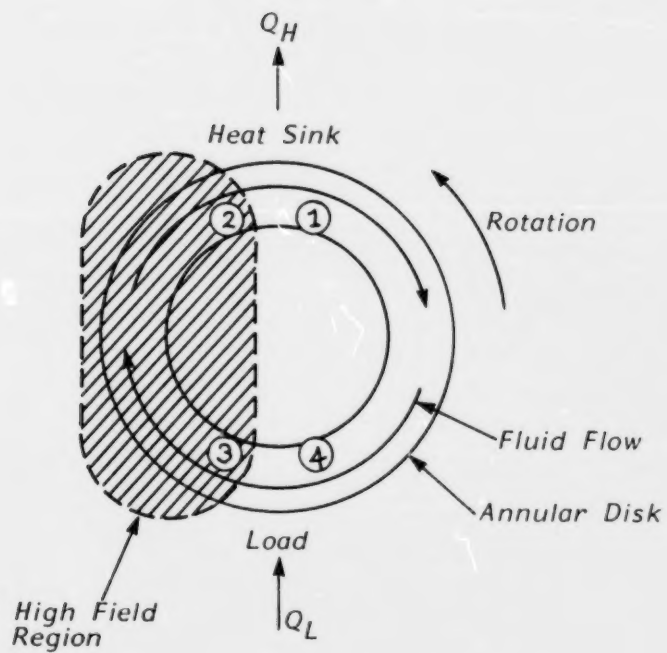


7a. Heat Pump Schematic

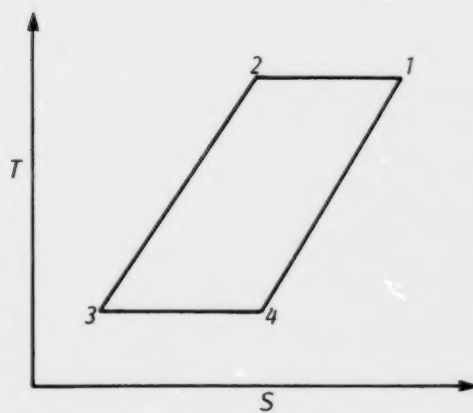


7b. T-S Diagram For Material

FIGURE 7a&b
ROTARY BRAYTON CYCLE MAGNETIC HEAT PUMP



7c. Heat Pump Schematic



7d. T-S Diagram For Material

FIGURE 7c&d
ROTARY ERICSSON CYCLE MAGNETIC HEAT PUMP

1. The magnetic material at point 1 moves into the field at point 2, undergoing an adiabatic magnetization. At the same time, fluid moving from point 2 to 1 gives up its heat to the external sink.
2. As the material moves from point 2 to 3, in the constant magnetic field, it gives up its heat to the fluid moving from 3 to 2.
3. In passing from point 3 to 4, the material undergoes an adiabatic demagnetization, cooling it. It absorbs heat from the fluid passing from 4 to 3, i.e. from the low temperature heat source.
4. Moving from 4 to 1, the material is heated against the regenerator fluid, completing the cycle.

Rotary magnetic heat pumps can also operate on the Ericsson cycle as shown in Figure 7c. The differences between the Ericsson system and the above are that the regenerator fluid flows through the material during field changes so the magnetizations and demagnetizations are isothermal rather than adiabatic. Heat is given up to the internal heat sink during the isothermal magnetization 1→2 and absorbed from the internal source during the isothermal demagnetization 3→4. The other two segments are regenerative as in the Brayton cycle.

The reciprocating system devised by Brown operates on a Stirling or Ericsson cycle. It consists of a vertical column of liquid (the regenerator) with the magnetic material moved within it by an actuator. The magnetic material is in a form that allows the fluid to pass through it easily while making good thermal contact for heat transfer. The magnetic coil is able to move with the magnetic "core" so as to maintain a constant field as the core moves within the column. The process is as follows (refer to Figure 8a)/6/:

1. The magnetic field is turned on with the core at the top of the column, which warms the core.
2. The core and the coil are moved together down the column with the magnetic field on, maintaining a constant field. The core gives up its heat to the liquid on the way down.
3. At the bottom of the column, the magnetic field is turned off, cooling the core.
4. The cooled core and the coil are then raised back through the column with the field off. The core absorbs heat from the lower section of the liquid column. When the core reaches the top of the column, it is warmer than it was at the start because it absorbs heat from the warmed liquid at the top.

When the desired temperature gradient has been attained, after a number of cycles, the warmed or cooled liquid can be circulated through heat exchangers. Alternately, continual heat flow can be obtained by heat exchangers attached to the column which restore the column to its original state after each cycle. Figure 8b shows one possible configuration for a reciprocal heat pump/6/.

Magnetic heat pumping offers significant advantages for industrial applications. Some of these are:

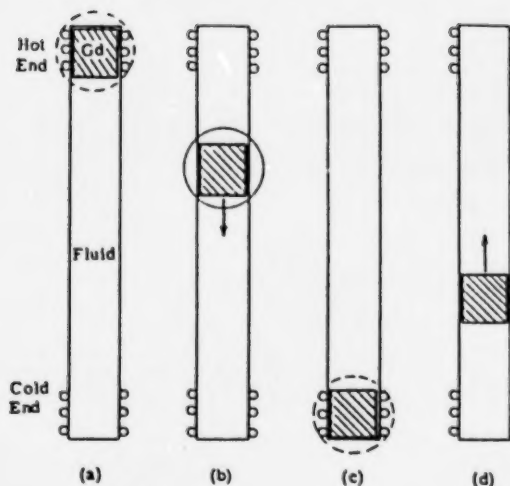


FIGURE 8a

REGENERATIVE MAGNETIC CYCLE. SOLID CIRCLE REPRESENTS FIELD ON. DOTTED CIRCLE IN (a) REPRESENTS FIELD INCREASING; IN (c), FIELD DECREASING. THE PROCESSES ARE (a) ISOTHERMAL MAGNETIZATION, (b) CONSTANT FIELD COOLING IN REGENERATOR FLUID, (c) ISOTHERMAL DEMAGNETIZATION, AND (d) ZERO (OR LOW) FIELD WARMING IN REGENERATOR

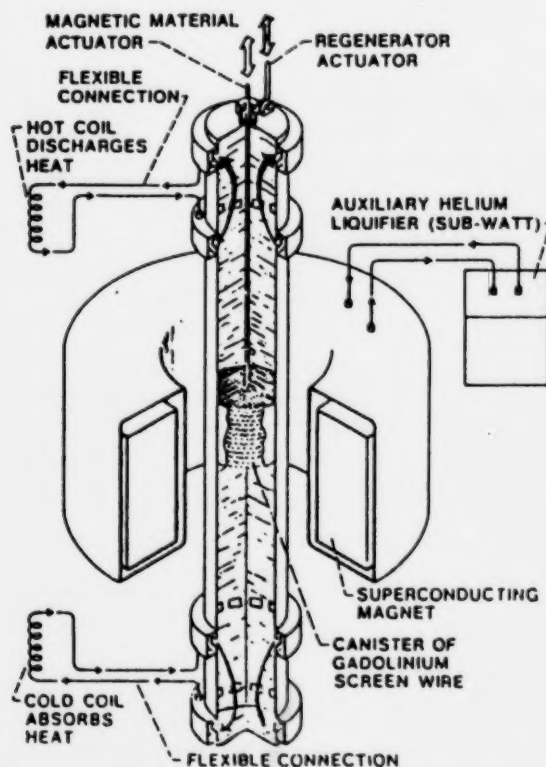


FIGURE 8b

POSSIBLE CONFIGURATION OF A RECIPROCAL MAGNETIC HEAT PUMP

- Flexibility. A number of different thermodynamic cycles can be utilized, and materials exist for almost any working temperature.
- Efficiency. Magnetic cycles can approach Carnot efficiencies. With improved superconducting magnets, efficiencies should increase and temperature ranges become larger. Heat transfer is essentially the only irreversible process in the cycle.
- Simplicity. Cycle speeds are low and no gaseous fluids are involved, so there are few moving parts and no high pressure equipment is needed.

The disadvantages of this type of heat pump are the expense of the fairly exotic materials like gadolinium needed for use around room temperature and the need for superconducting magnets to attain the high magnetic fields required. The second disadvantage is not major, however, as the helium refrigerator needed to cool the coil is not large.

3.0 CHEMICAL HEAT PUMPS

There are two types of absorption cycles: the vapour absorption heat pump (VAHP), sometimes referred to as type 1, and the vapour absorption heat transformer (VAHT), sometimes referred to as type 2. One of the major differences between the two absorption cycles is the internal pressure distributions in the system. The VAHP has a higher pressure in the condenser than the evaporator, while the VAHT has a lower pressure in the condenser than in the evaporator. This difference in pressures allows the absorption heat pump to be useful for a broad range of evaporator and condenser temperatures. The details of each of the two cycles are outlined in the following paragraphs.

Chemical heat pumps use chemical processes, such as solution/dilution, absorption, etc., to upgrade the temperature of waste heat. Heat pumps are classified into two categories, heat of mixing and heat of reaction. Heat of mixing chemical heat pumps use the energy liberated during sorption of one compound by another. The processes which are included as heat of mixing are absorption, adsorption, and solution/dilution. Heat of reaction heat pumps use the energy released when new chemically stable compounds are formed by electron sharing or transfer. Heat of reaction heat pumps have gained very little attention in the past, but are considered as showing a great potential for industrial applications in the future because higher heats are involved than in heat of mixing heat pumps. Both of the two categories will be discussed in the following paragraphs.

3.1 Absorption Heat Pump

In the heat of mixing category, the absorption heat pump (AHP) has received the most research attention. The principle of the absorption cycle, shown in Figure 9/11/, is as follows:

1. Waste heat is used to evaporate the refrigerant in the evaporator.
2. The solvent in the absorber, which has an affinity for the refrigerant, then draws the refrigerant vapour from the evaporator into the absorber, where it is absorbed by the solvent.
3. The pressure of the strong solution is then increased by a liquid pump and the strong solution is passed to the generator.
4. In the generator, heat is added to evaporate the refrigerant out of the solution.

5. The solvent (weak solution) is returned to the absorber ready to begin a new cycle.
6. Meanwhile, the hot refrigerant vapour passes from the generator to the condenser, where it releases latent heat to the sink while condensing back to a liquid.
7. Finally, the refrigerant passes through a pressure reducing valve, and returns to the evaporator to begin a new cycle.

Since absorption heat pumps work mainly with thermal energy, they are free from mechanical vibrations and noise problems. Also, the thermal efficiency of absorption heat pumps remains constant under varied conditions, whereas a mechanical heat pump's thermal efficiency (COP) is dependent on the temperature difference between the source and the sink. These attributes make AHP very attractive to industry/11/.

An example of an application for a VAHP is to recover heat from a distillation column, as shown in Figure 10/12/. Figure 11a displays the conventional system of heating the product by heat exchanging with steam from a boiler, and cooling the distillate with cooling water. Figure 11b shows a modified distillation tower using a VAHP to recover heat from the distillate and return it to the process fluid. The process is as follows: heat is removed from the distillate into the evaporator, while high grade energy from steam is added to the generator. The heat released from the absorber and the condenser is then returned to the product, instead of being dissipated uselessly.

Another example is a VAHP used for district heating at Trollhattan, Sweden/13/. It began operation in December of 1984 and is the largest absorption heat pump in the world, producing approximately 7 MW of useful heat. Hydrogen, a by-product from a nearby manufacturer of chlorates, is used to fire a boiler which produces steam to heat the generator. The working fluid pair is lithium bromide and water.

The VAHT is a relatively new form of absorption heat pump, compared to the VAHP. The VAHT, shown in Figure 11/11/, utilizes strictly waste energy streams for the evaporator and generator, and delivers high temperature heat at the absorber. The heat delivered at the absorber is at the highest temperature in the system. In this way, the VAHT differs from the VAHP, which delivers heat at the mean temperature of the system. This temperature "boosting" is the main benefit of the VAHT over the VAHP. The VAHT using lithium bromide - water working fluids can reach delivery temperatures as high as 150°C.

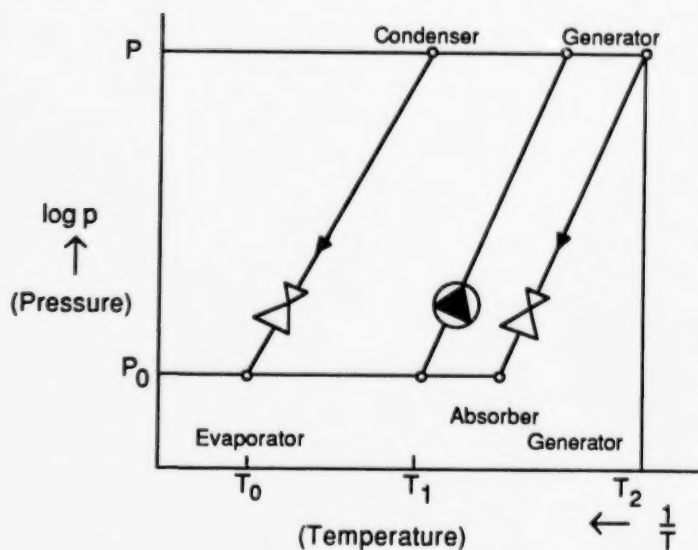
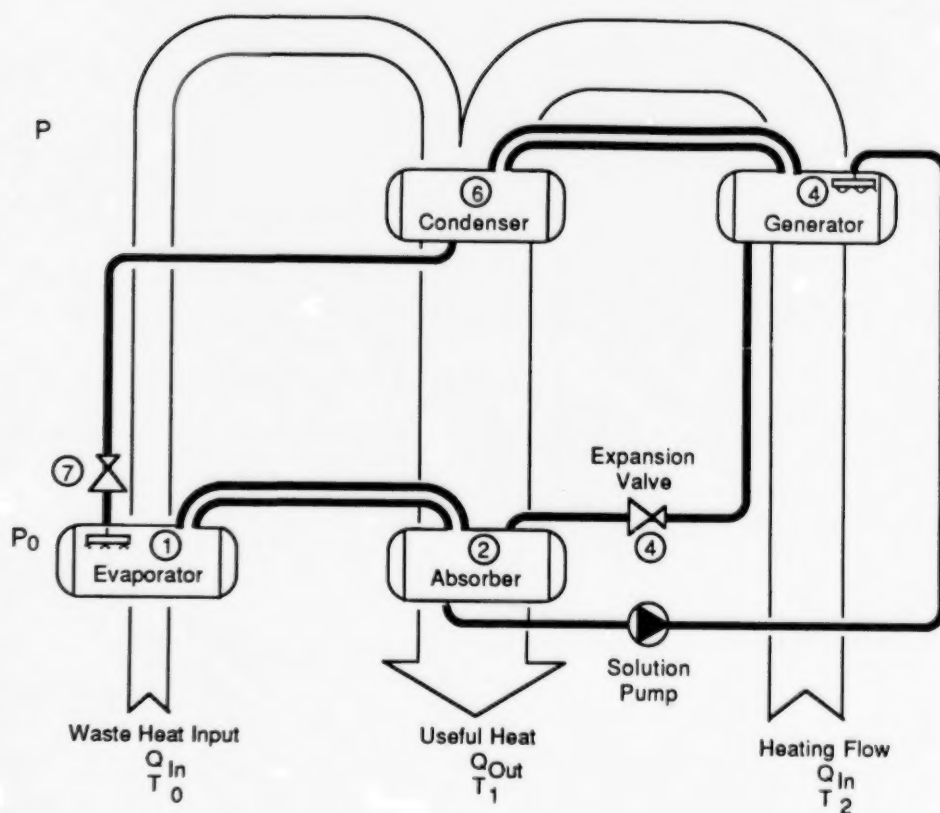


FIGURE 9
ABSORPTION HEAT PUMP

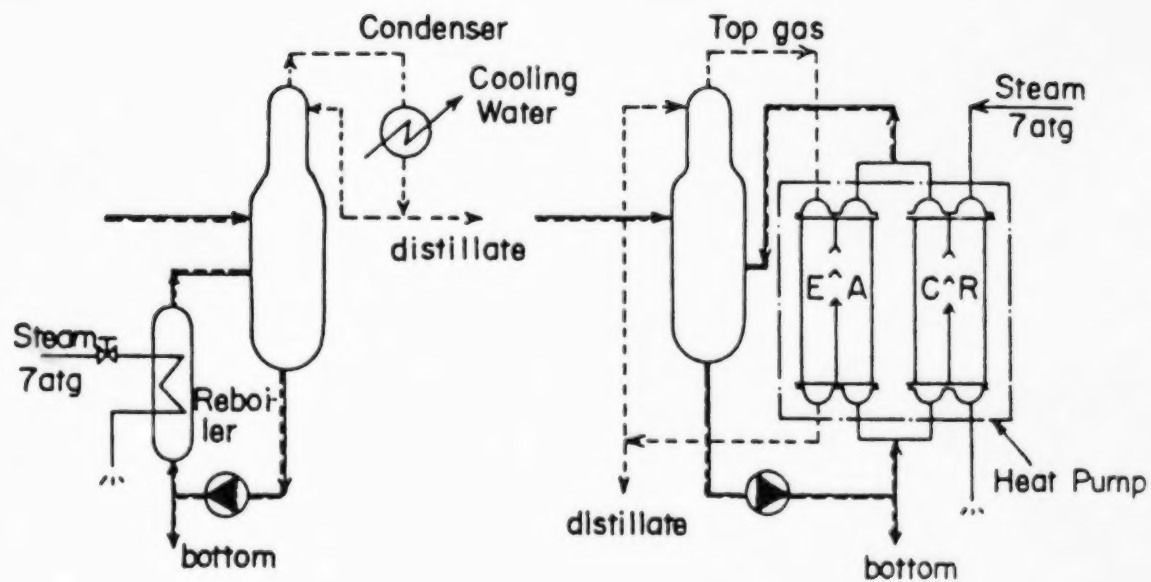


FIGURE 10
APPLICATION OF A VAHP

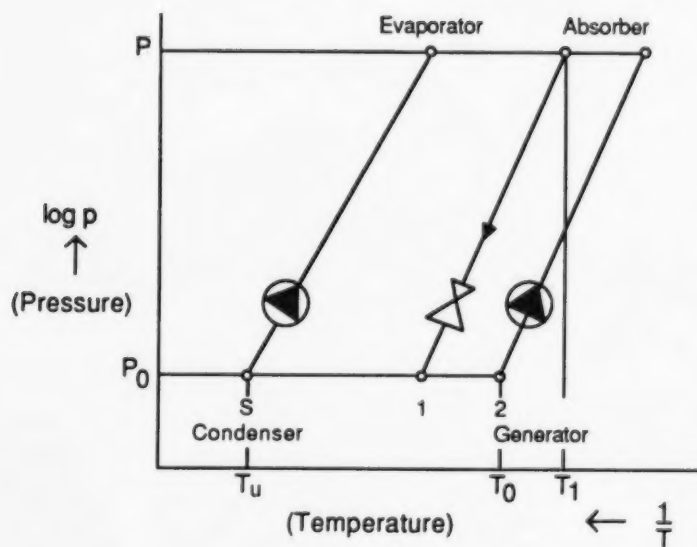
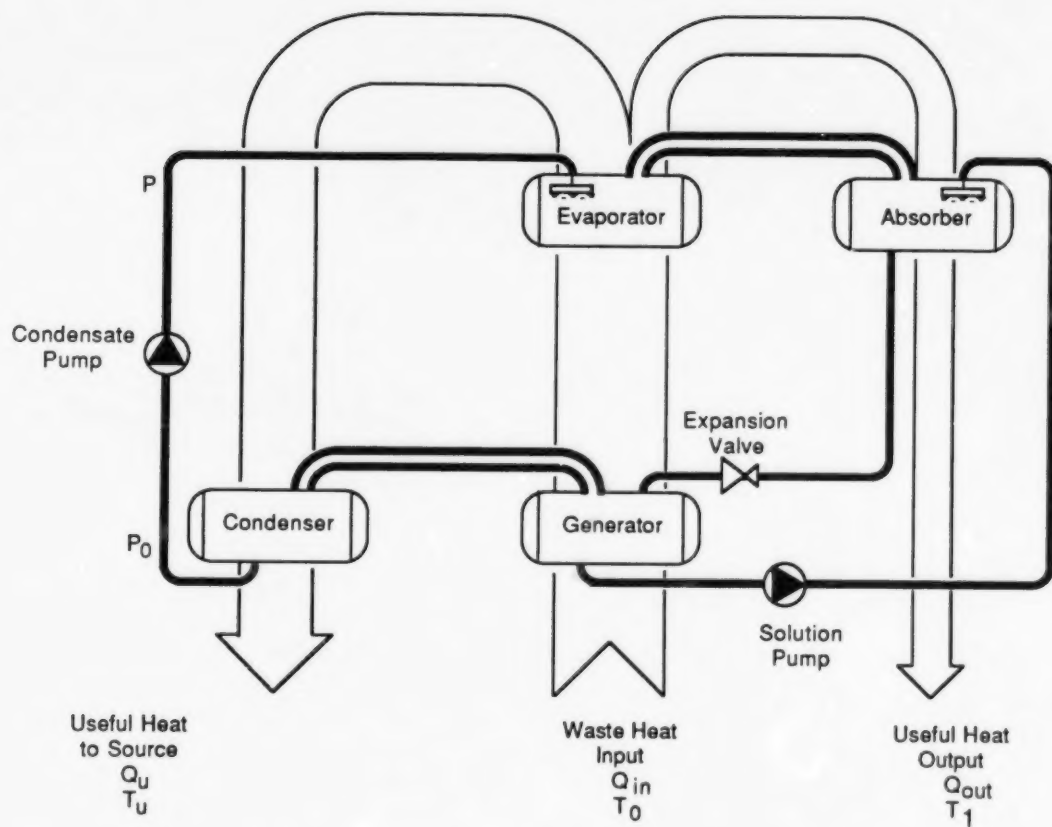


FIGURE 11
VAPOUR ABSORPTION HEAT TRANSFORMER

One application of a VAHT is recovering waste heat from cooling water to preheat boiler feed water in a rubber manufacturing facility. Prior to installation of the heat pump, hot cooling water was simply discharged from the plant. The VAHT system, as shown in Figure 12/12/, utilizes the hot water from the plant as a heat source for the generator and the evaporator. The higher temperature heat is then returned at the absorber to heat boiler feed water and reduce boiler fuel consumption.

As with mechanical heat pumps, research into absorption heat pumps is being performed to identify better pairs of working fluids. Some of the current refrigerant/absorber pairs being used or studied are: lithium bromide/water, R22/DMF (dimethyl formamide), lithium chloride/water, ammonia/water, zeolite/water, and sodium hydroxide/water/14/.

3.2 Adsorption Heat Pumps

Adsorption heat pumps operate similarly to absorption heat pumps. Adsorption is the condensation of gases, liquids, or dissolved substances on the surfaces of solids. Methanolated salt systems are currently being researched, with such salt/solvent pairs as calcium chloride/methanol and nickel chloride/methanol. In the nickel chloride/methanol adsorption heat pump, waste heat is used to separate the salt from methanol at temperatures between 40°C and 100°C, and then returned during the recombination process in the absorber at temperatures between 30°C and 130°C. The nickel chloride/methanol working pair combination has been considered for the production of hot water/15/.

3.3 Solution/Dilution Heat Pumps

In a solution/dilution heat pump, the heat transfer is driven by the exothermic dilution of water into an acid. The sulphuric acid/water heat pump is an example of this technique of heat pumping, shown schematically in Figure 13/16/. It is composed of six basic components: an evaporator, an absorber, a generator, a condenser, and 2 heat exchangers. Referring to Figure 13 the process is as follows:

1. Waste heat (approximately 30 to 50% of entire input) is used to heat a strong acid solution.
2. Warm waste water is input into the evaporator where water vapour is produced. The water vapour then travels to the absorber where it comes into contact with the warm strong acid solution.
3. The water vapour is absorbed into the acid solution where the resulting absorption process releases the sum of the heat of dilution and the heat of vapourization to warm the dilute acid by approximately 20°C to 80°C.
4. The hot acid/water solution is heat exchanged with the sink, releasing high temperature sensible heat.
5. The water is flash distilled out of the acid and passed to the condenser. The resulting strong acid solution is passed on to point 1 where the acid begins a new cycle. Meanwhile, the water vapour passed to the condenser is condensed by industrial water or ground water prior to being dumped or returned to the evaporator.

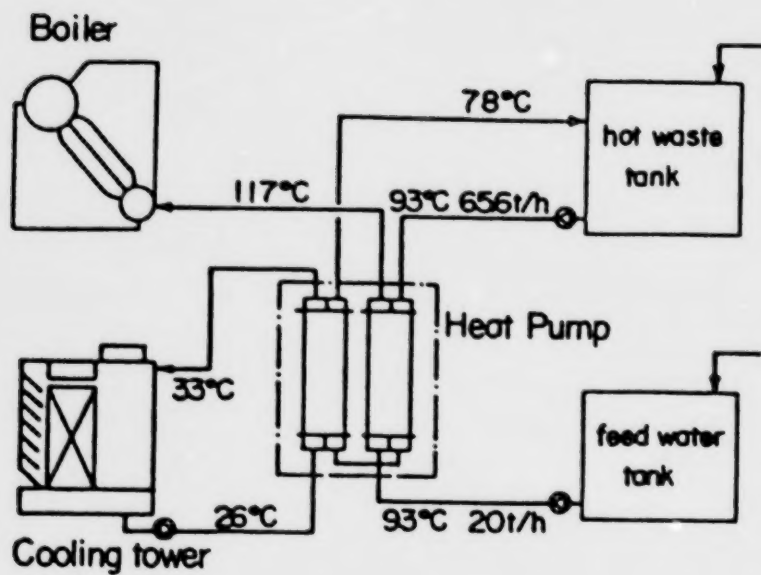


FIGURE 12
FLOW AND SPECIFICATIONS FOR PRACTICAL
APPLICATION IN A RUBBER FACTORY

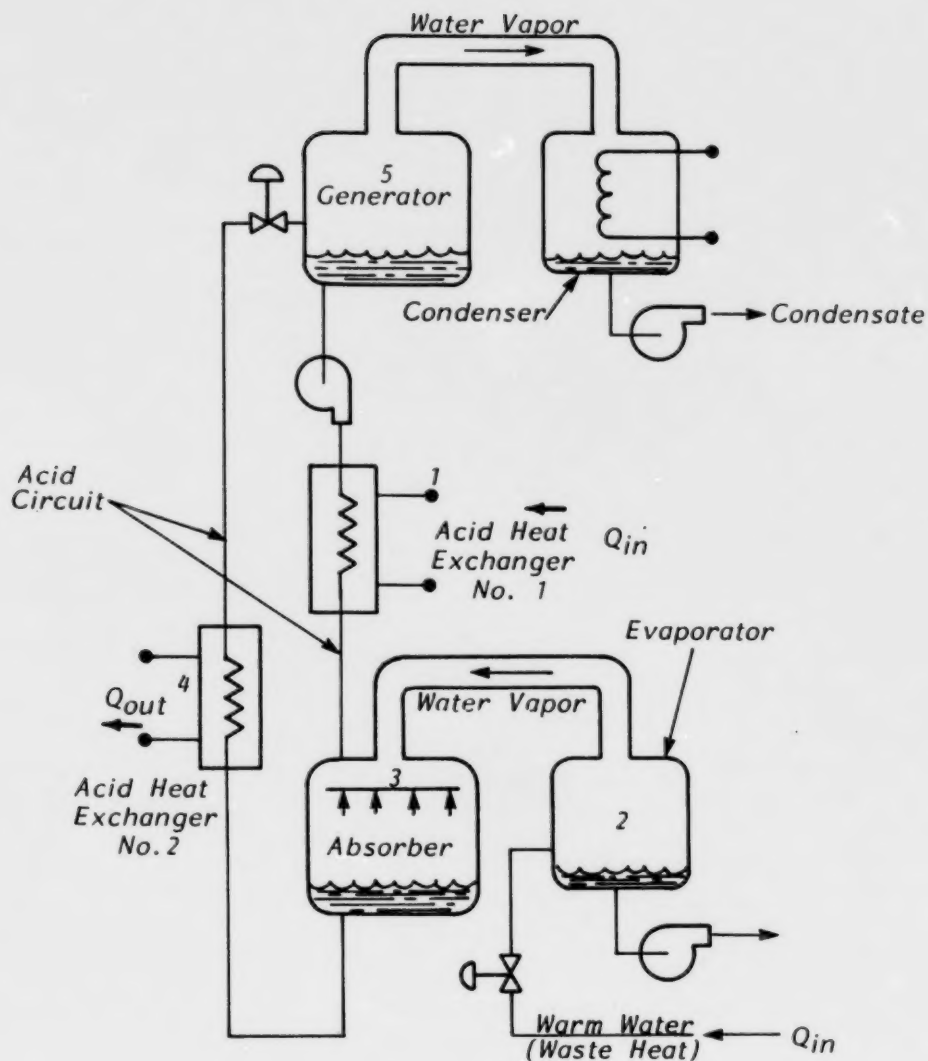


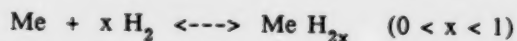
FIGURE 13
SOLUTION/DILUTION SULPHURIC ACID/
WATER CHEMICAL HEAT PUMP

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Sulphuric acid solution/dilution heat pumps are already produced commercially with delivery temperatures between 66°C and 240°C. Typical thermal efficiency values range from 0.1 to 0.5. Due to the high corrosiveness of the acid at the elevated temperatures involved, glass lined heat exchangers are required.

3.4 Metal Hydride Heat Pumps

When a crystalline metal absorbs hydrogen gas in the reversible reaction/17/



to form a metal hydride, large amounts of heat can be released. This hydriding reaction, along with the reverse dehydriding reaction, can be used in a heat pump cycle. The advantages of using this reaction in a heat pump are/18/:

- Hydriding is reversible,
- Hydriding is an exothermic reaction,
- Dehydriding is an endothermic reaction, and
- Hydrogen diffuses rapidly within hydrides.

Also, at constant temperature, the pressure of the hydrogen over the hydride remains nearly constant over a range of values of the ratio H/M, where H is the number of hydrogen atoms, and M the number of metal atoms, in the hydride (see Figure 15)/19/.

When two different metal alloys are used as a working pair, with the hydrogen gas as the heat transfer fluid, the reaction can be used as a heat pump.

The advantages of hydride heat pumps are/17,18/:

- quiet operation,
- no moving parts,
- no toxic gases or fluids,
- Adaptable to various temperatures and applications.

The ideal thermodynamic cycle for a hydride heat pump consists of four steps as shown in the P vs. H/M and T vs. H/M graphs in Figures 16 and 17/19/. The dashed lines are for the low-temperature hydride B and the solid lines are for the high-temperature hydride A. The four steps are/19/:

- 1->2: High temperature isothermal heat addition.
- 2->3: Sensible cooling.
- 3->4: Low temperature isothermal heat addition.
- 4->1: Sensible heating.

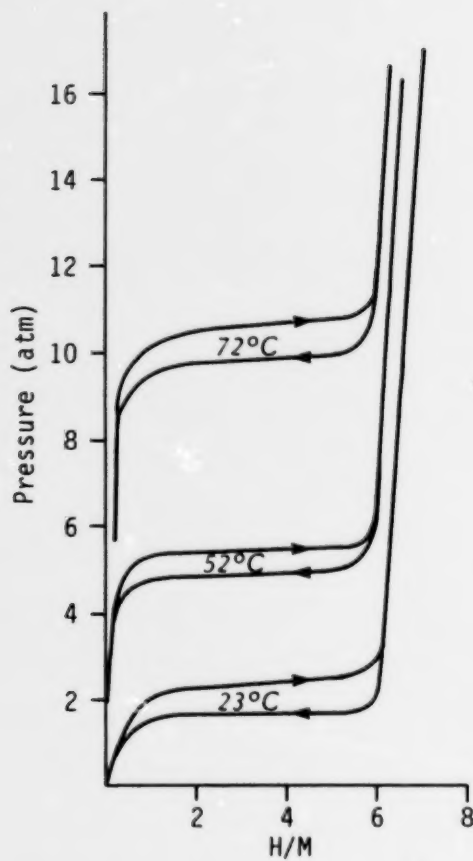


FIGURE 14
ABSORPTION/DESORPTION ISOTHERMS FOR LaNi_5

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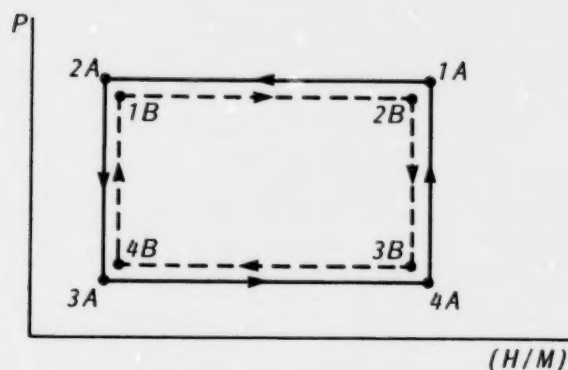


FIGURE 15
IDEALIZED HEAT-PUMP CYCLE ON P vs (H/M) COORDINATES

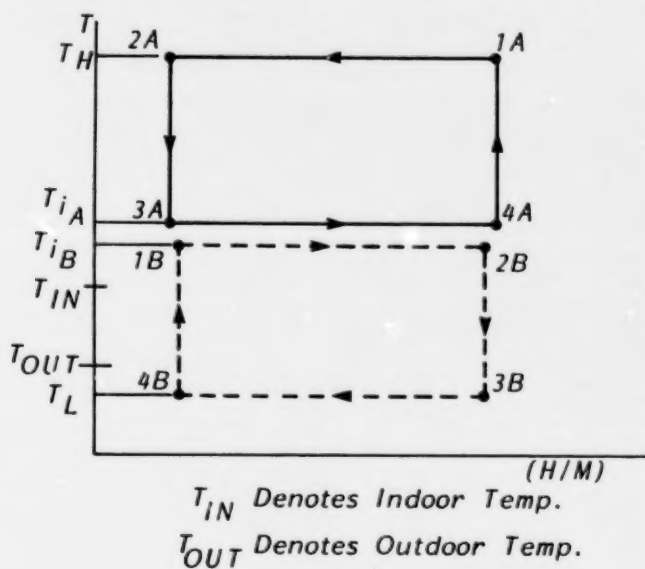


FIGURE 16
IDEALIZED HEAT-PUMP CYCLE ON T vs (H/M) COORDINATES

Each of these processes is described for the ideal heating mode in the following four paragraphs/19/ (see also Figure 18)/20/:

- 1->2: In this process, a quantity Q_H of heat at high temperature T_H is transferred to the vessel containing hydride A. This causes desorption of hydrogen from A at temperature T_H . This hydrogen flows to the vessel containing hydride B, where it is absorbed, liberating heat isothermally at temperature T_{iB} which is rejected to the area to be heated.
- 2->3: The temperature of hydride A is then decreased from T_H to T_{iA} while that of hydride B is decreased to T_L from T_{iB} . No hydrogen transfer is allowed between the vessels during this process.
- 3->4: Heat, Q_L at a low temperature T_L is then transferred to the vessel containing hydride B. This heat can come from the waste heat stream. The heat addition causes hydrogen desorption from B at a temperature T_L . The hydrogen flows to the vessel containing A, where it is absorbed. This causes heat at temperature T_{iA} to be released from A which is used for heating.
- 4->1: Finally, hydrides A and B are returned to their initial states by heating them to temperatures T_H and T_L , respectively. No hydrogen transfer between the vessels is allowed.

In its most basic form, a hydride heat pump consists of two vessels containing the metal or metal hydride, connected by a tube to carry the hydrogen gas (see Figure 19)/19/. The tube has a filter to prevent the hydrides from mixing while passing the hydrogen gas. It should also have a low heat conductivity to prevent conduction of heat between the vessels. The vessels themselves must have some method of enhancing heat transfer between the hydrides and the external heat transfer fluid (air or water). The metal alloys themselves are in powdered form to increase the reactivity of the metals with the hydrogen gas.

The selection of the metal hydrides depends on the mean temperature of operation and temperature range desired. Hydrides must be selected which have fairly flat plateaus on the P vs. H/M plot. The vertical distance between the hydriding and dehydriding plateaus (caused by hysteresis) should be as small as possible (see Figure 15). Cost and availability are also important factors. Some alloys that have been tested are FeTi, LaNi₅, and MnNi₅. The best materials that have been found are of the type AB₅, where A is a rare-earth element like La and B is a transition metal like Ni./18/

Southern California Gas of Los Angeles has done work under a contract from Brookhaven National Laboratories on finding an optimal design for a metal hydride heat pump/18/. Also, Daimler-Benz of Germany has done research into preheating engines and/or passenger compartments in cars and buses using this technology/17/.

4.0 OTHER HEAT PUMP TECHNOLOGIES

Some types of heat pumps do not fit into either the mechanical or the chemical category. One example of this, the Peltier or thermoelectric heat pump, is described in the following paragraphs.

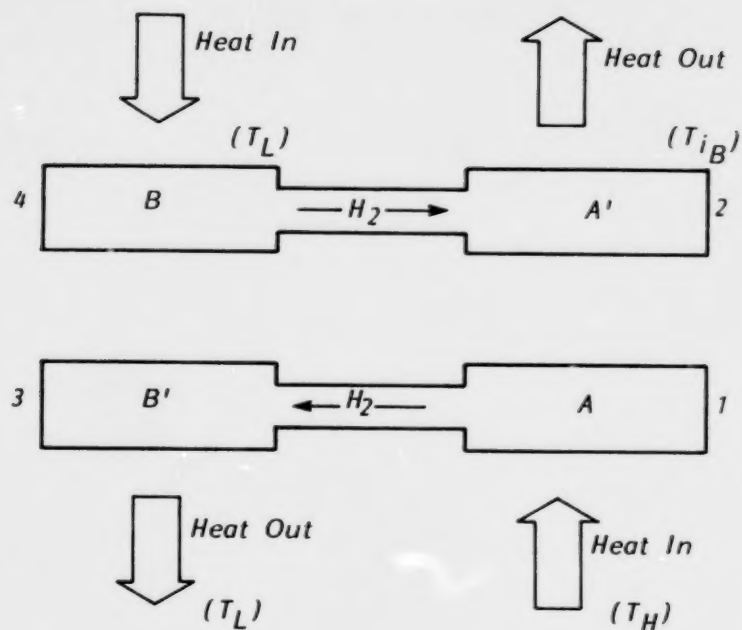


FIGURE 17
A SCHEMATIC DIAGRAM OF A HYDRIDE HEAT PUMP

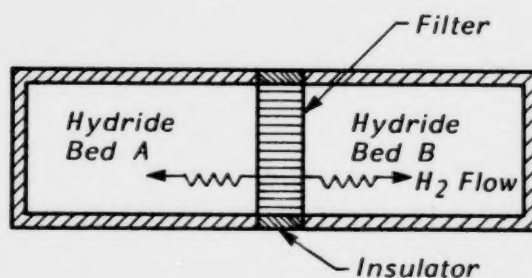


FIGURE 18
SCHEMATIC OF HYDRIDE TUBE

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4.1 Peltier (Thermoelectric) Heat Pumps

The Seebeck, or thermoelectric, effect has been used for many years in thermocouples. It is the effect that when two dissimilar metals are joined in a circuit, current will flow if the two junctions are at different temperatures. The reverse of this effect, the generation of or absorption of heat when current is applied to the above circuit, is called the Peltier effect. It can be used as the basis of a heat pump/22/.

All Peltier heat pumps on the market use two differently doped semiconductors as the dissimilar metals. One p-type and one n-type semiconductor joined in series is called a couple. A number of couples in series is the main element in a Peltier heat pump. There is also some type of heat exchanging system attached to each end of the module to facilitate efficient heat transfer (see Figure 19a and 19b)/23/.

Figure 20/23/ is a schematic of a one-couple heat pump module to demonstrate the principles of operation. When the current is flowing in the conventional positive (+) to negative (-) direction, the upper junction becomes colder and the lower, hotter. If the cold junction is thermally coupled to a waste heat stream and the hot terminal to the heating application, the couple can be used to upgrade waste heat or for refrigeration.

As the number of couples increases, the amount of heat that can be transferred also increases. As of 1981, Peltier heat pumps had been built with capacities up to 35.2 kW (10 tons) of air conditioning/23/.

The temperature upgrading capacity has increased significantly as semiconductor technology has improved. Figure 21/23/ shows the maximum temperature differences obtained over the last 150 years.

This technology has been used primarily for small scale cooling applications. Due to the cost of semiconductors and the fairly precise manufacturing techniques required, large scale industrial usage has been minimal. Large-scale Peltier heat pumps have been used in specialized applications by the U.S. Military and Space Programmes, however, because of factors like portability, quiet operation, compactness, and ability to operate in any orientation and in zero- or high-gravity conditions.

The main disadvantage of Peltier heat pumps as compared to more conventional systems is their low COP's. Most Peltier heat pumps have COP's between 1 and 2, with the average about 1.5. Recent research in France using sintered pellets in columns/24/ has reported attaining a COP of 3.2 using bismuth as the semiconductor material. Figure 22/23/ shows theoretical maxima for COP values as a function of temperature difference and figure of merit. Figure of merit (Z) is an important number in semiconductor physics which depends on the material's conductivity, resistivity, and Seebeck coefficient. The higher the value of Z , the better the couple's performance. As of 1980, materials are available with Z 's on the order of $0.003/^{\circ}\text{C}$.

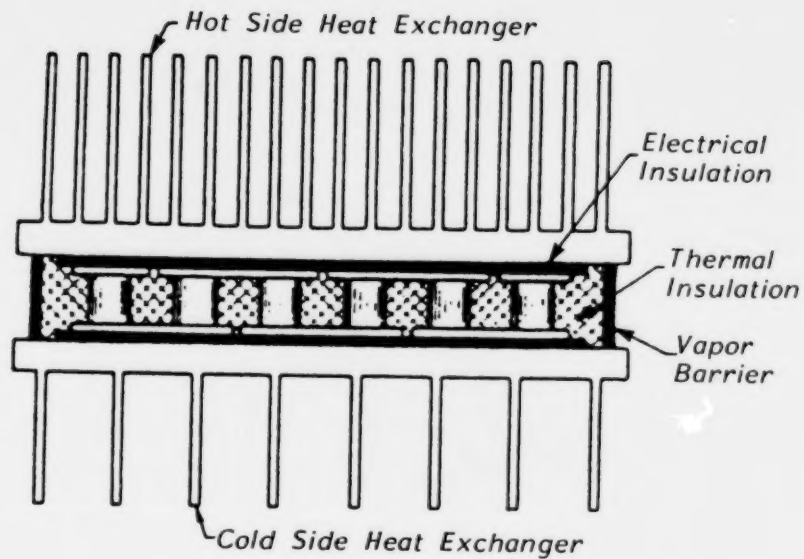


FIGURE 19a
CROSS SECTION OF THERMOELECTRIC MODULE AND
HEAT TRANSFER SURFACES

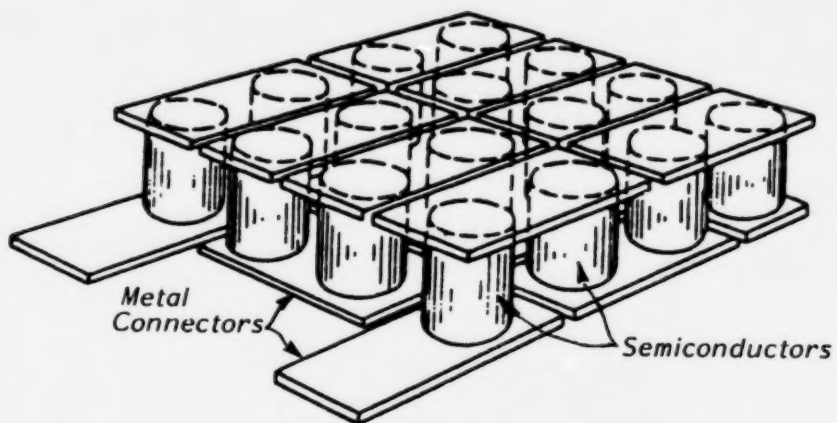


FIGURE 19b
TYPICAL THERMOELECTRIC MODULE

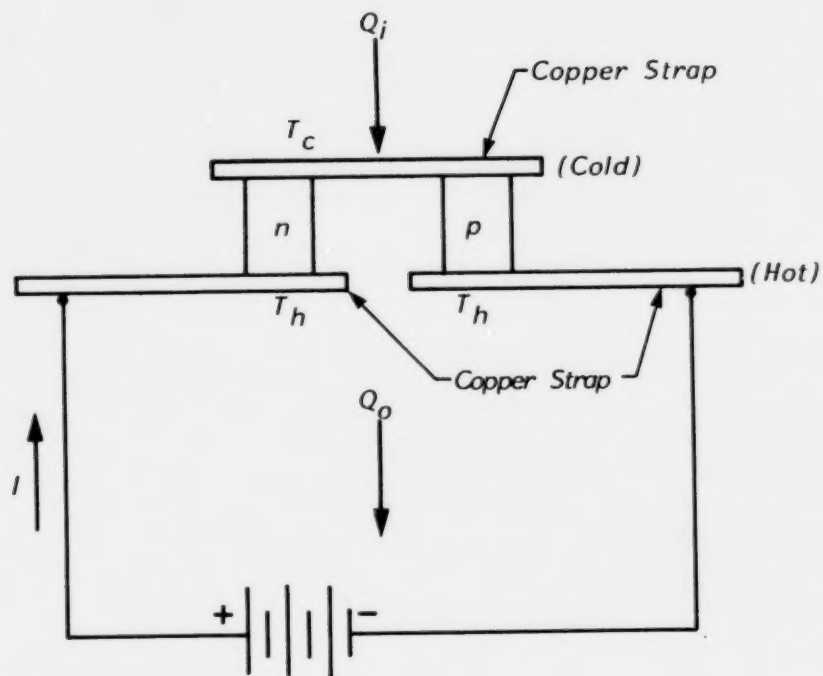


FIGURE 20
ONE COUPLE THERMOELECTRIC HEAT PUMP

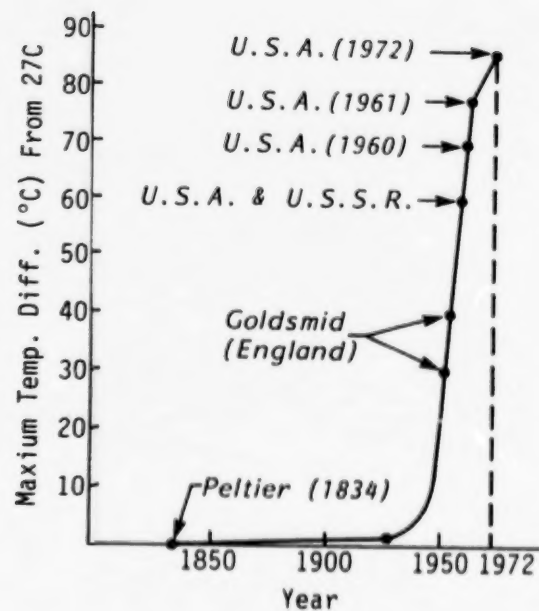


FIGURE 21
IMPROVEMENTS IN MAXIMUM TEMPERATURE DIFFERENCE ACHIEVED
WITH A THERMOELECTRIC COUPLE OVER THE YEARS

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5.0 HEAT PUMP PERFORMANCE AND APPLICATION RANGE

In this section, a general overview of the performance and application range all the technologies discussed is given. All graphs except one show COP as a function of either sink temperature, source temperature, or temperature boost. The exception to this is magnetic heat pumps, for which this type of data is unavailable. The boundaries for each heat pump type are fairly indistinct, and most are expanding as the technology improves, so these charts should only be used as a rough guide. Also, COP is defined differently in some cases. For each Figure, the definition used is given.

Figure 23/5/ is a plot of COP against sink temperature for a Brayton cycle compression heat pump. The inlet temperature varies from 65 to 150°F, while the outlet temperature ranges from 150 to 350°F. The refrigerant fluid is air.

Figure 24/11/ is a plot of COP against the source temperature for a closed-cycle Rankine compression heat pump. The refrigerant fluid is one of the Freon types, (typically R22, R12, or R114). The curves are not greatly affected by the choice of refrigerant.

Figure 25/25/ shows the efficiency as a percent of Carnot efficiency of a magnetic heat pump as a function of heat pumping capacity. COP values at temperatures of interest to industry are not available as it is a fairly new technology and has been used mainly at cryogenic temperatures. The working material for both types is gadolinium, and the refrigerant fluid is water.

Figure 26/16/ is a plot of heating COP as a function of temperature boost for a solution/dilution heat pump. The pump is operating between a heat source at 54 to 121°C and a heat sink at 66 to 193°C. The heat pump uses sulphuric acid and water as the reagents.

Figure 27a/26/ and 27b/11/ show the COP's of absorption heat pumps as functions of temperature boost and median source temperature (temperature of heat supplied to the generator), respectively. Figure 28a is for LiCl - water and LiBr - water systems, while Figure 28b is for LiBr - water. The pumps are operating between similar temperature limits in the two graphs.

Figures 28a and 28b/14/ are plots of COP against source temperature for a double and single stage vapour absorption heat transformer, respectively. The source temperatures range from 50 to 70°C, with condenser temperatures of 15 to 40°C. ΔX_a is the change in concentration of the solvent across the absorber.

Figure 29/27/ shows COP as a function of sink temperature (T_H) for various source temperatures (T_L). The hydride pair is $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and LaNi_5 .

Finally, Figure 22/23/ shows the COP of the Peltier heat pump as a function of temperature boost and figure of merit, Z.

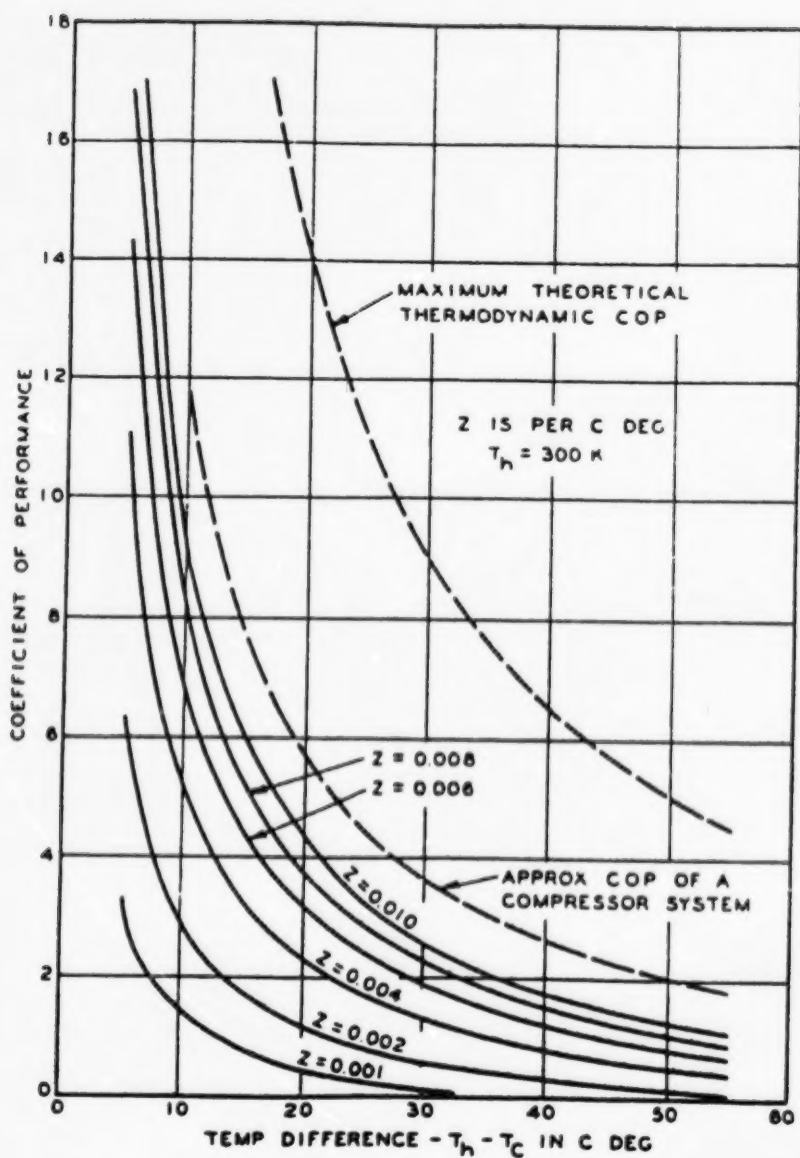


FIGURE 22
MAXIMUM COEFFICIENT OF PERFORMANCE OF A
THERMOELECTRIC COUPLE AS A FUNCTION OF TEMPERATURE
DIFFERENCE AND FIGURE OF MERIT, Z

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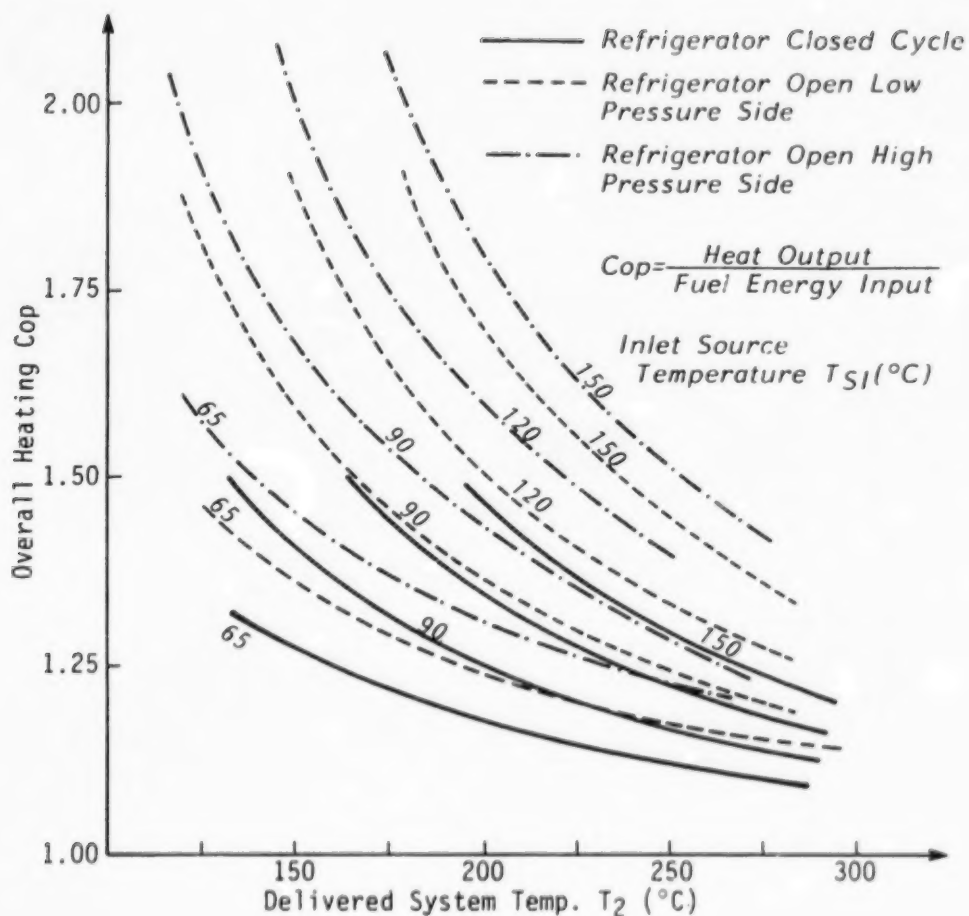


FIGURE 23
PERFORMANCE OF A BRAYTON CYCLE COMPRESSION HEAT PUMP

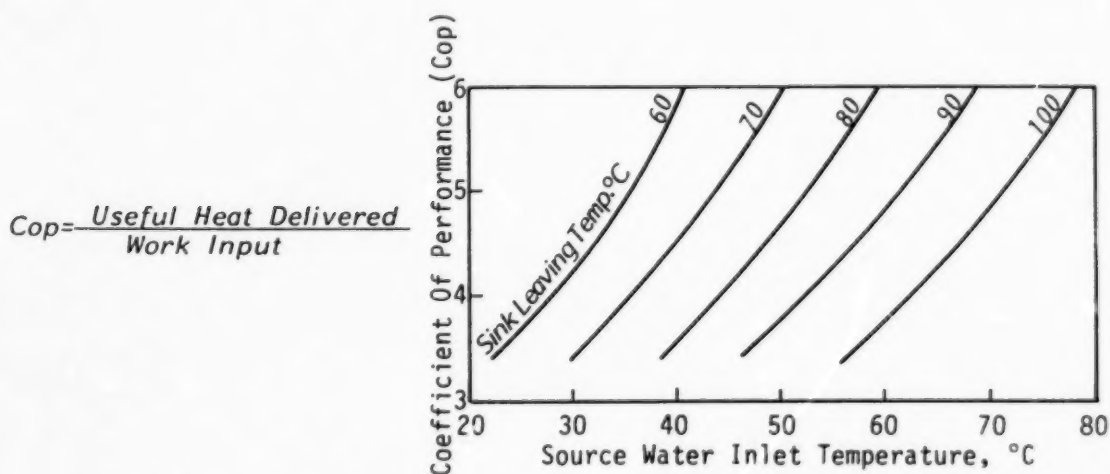


FIGURE 24
PERFORMANCE OF A RANKINE CYCLE COMPRESSION HEAT PUMP

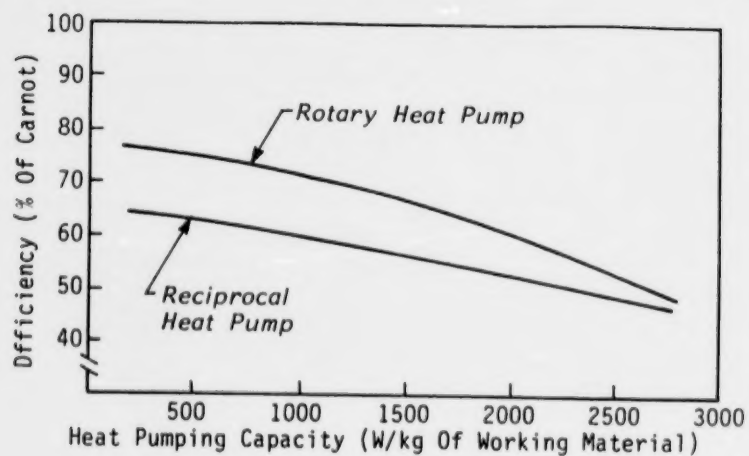


FIGURE 25
PERFORMANCE OF A MAGNETIC HEAT PUMP

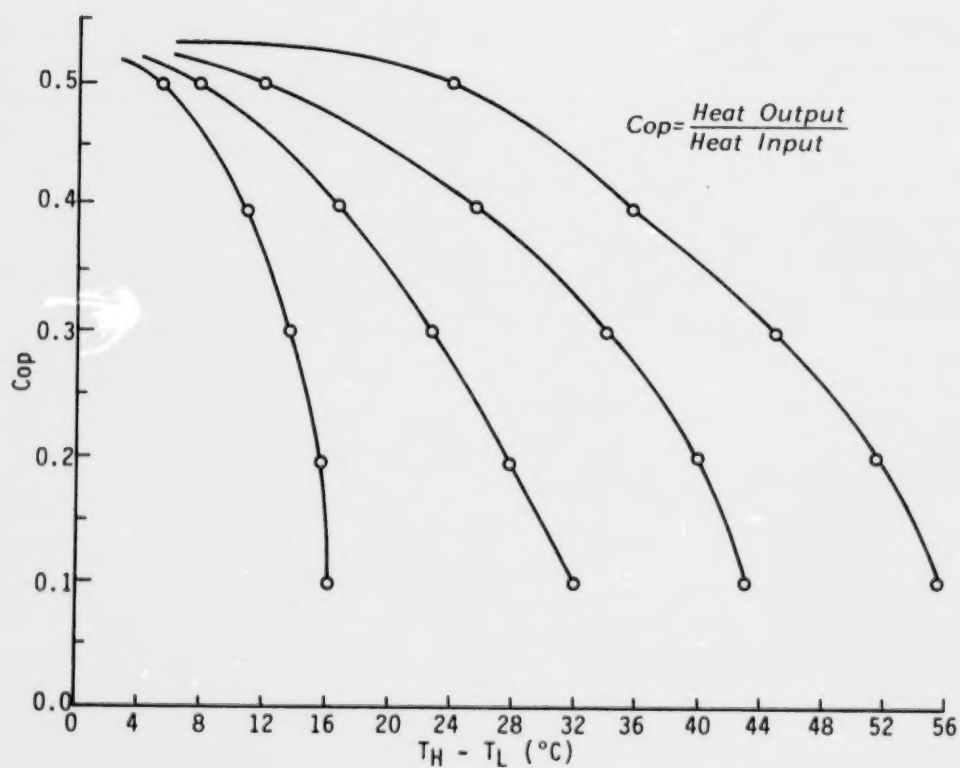
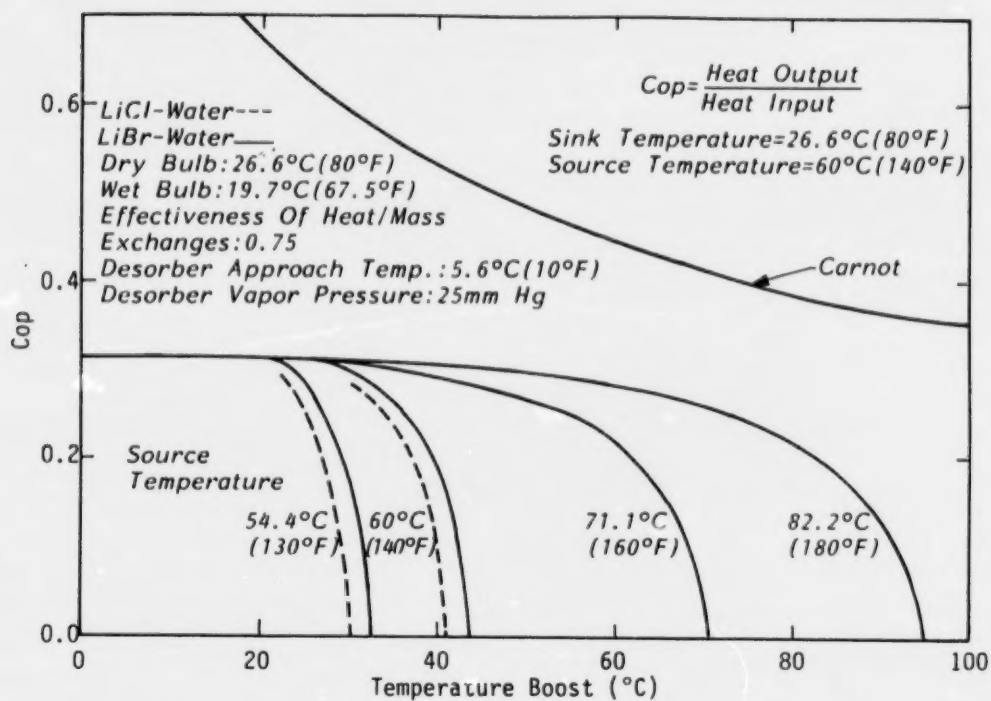


FIGURE 26
PERFORMANCE OF A SOLUTION/DILUTION HEAT PUMP



27a

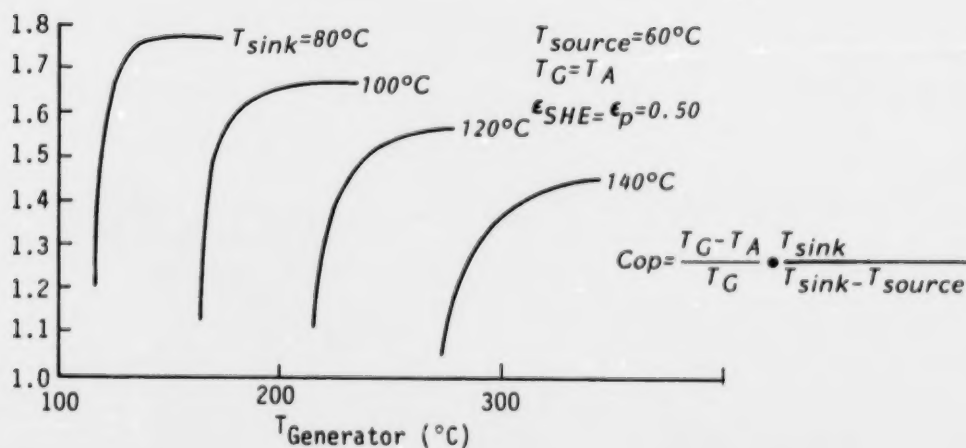
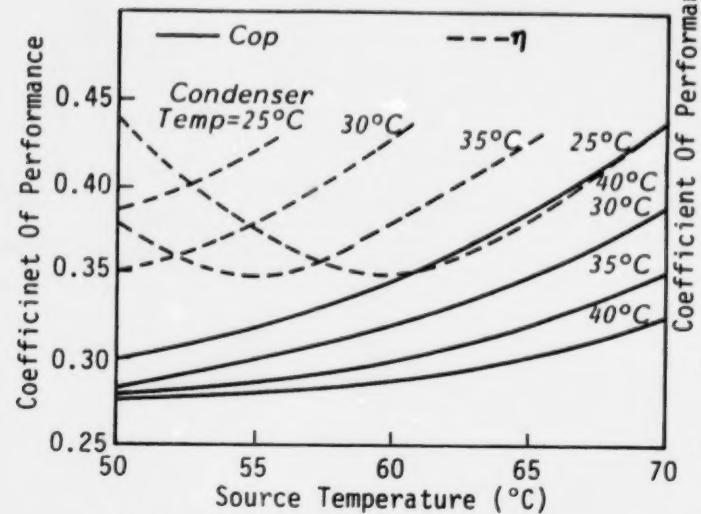


FIGURE 27b
PERFORMANCE OF AN ABSORPTION HEAT PUMP

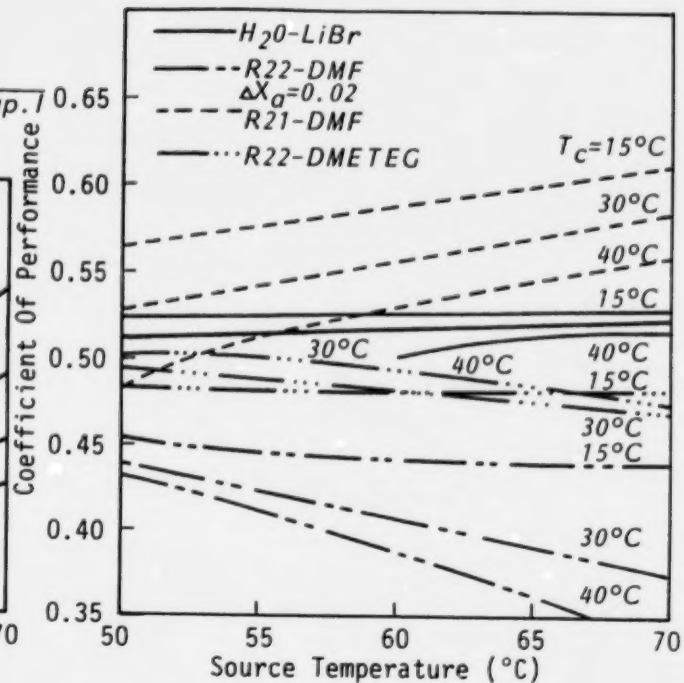
$$C_{op} = \frac{\text{Heat Out Of Absorber}}{\text{Heat Into Gen} - \text{Heat Into Evap.}}$$

$$C_{op} = \frac{\text{Heat Input To Abs. II}}{\text{Heat Into Gen. I} - \text{Heat Into Evap. I}}$$



I Stage: $H_2O-LiBr$ $\Delta X_a = 0.02$
II Stage: $R21-DMF$ $\Delta X_a = 0.02$

29a Double Stage



29b Single Stage

FIGURE 28
PERFORMANCE OF A VAHT

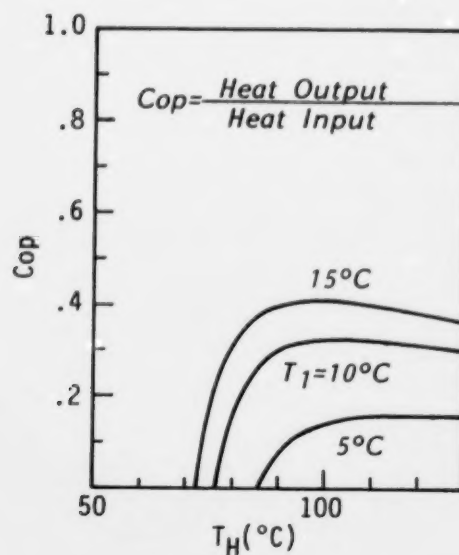
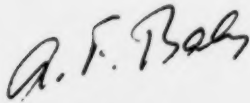


FIGURE 29
PERFORMANCE OF A METAL HYDRIDE HEAT PUMP

6.0 CONCLUSIONS

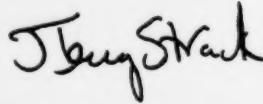
Research is continuing into finding methods to improve the technologies presented in this report. The lesser-established types of heat pumps, namely Magnetic, Metal Hydride, Solution/Dilution, and Peltier, are receiving most of the attention, as their potentials are high and their limits not yet firmly determined. Improved manufacturing methods and better understanding of the thermodynamic principles will doubtless bring about improvements in the COP and capacity of most of the heat pumps described in this report.

Approved:

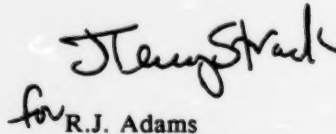


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